CRYSTAL AND MOLECULAR STRUCTURE OF 2e-DIETHYLAMINO-3e,4e-DIMETHYL-5e-PHENYL-2a-THIO-1,3,2-OXAZAPHOSPHOLANE

A. M. Gazaliev, M. Zh. Zhurinov,
O. A. Nurkenov, K. M. Turdybekov,
S. V. Lindeman, and Yu. T. Struchkov

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The results of an x-ray structural investigation of 2e-diethylamino-3e,4e-dimethyl-5e-phenyl-2a-thio-1,3,2-oxazaphospholane are discussed. It has been shown that the conformation of the 5-membered ring is that of a half-chair.

An x-ray structural study has been made of 2e-diethylamino-3e,4e-dimethyl-5e-phenyl-2a-thio-1,3,2-oxazaphospholane (I). The crystals of (I) are constructed from two independent molecules (IA) and (IB) having practically identical geometric parameters, as can be seen from Fig. 1* and Tables 1 and 2.

The conformation of the molecules is characterized by the departure of the pharmacopeal groups — the O1 and N1 atoms — in different directions from the plane of the benzene ring by 0.90 and 1.10 Å in (IA) and 0.93 and 1.01 Å in (IB). The torsion angle τ (C6C1C7O1) has values of 43.3(5) and 42.5(5)°, respectively and is close to the value (44°) in d-pseudoephedrine (II) [1]. The twisting around the C7—C8 bonds in (IA) and (IB) (the torsion angle ω (O1C7C8N1)) amounts to 32.8(4) and 31.8(4)°, which is appreciably smaller than in (II) and its hydrochloride (III) [1] (52 and 55°, respectively) because of the closure of the oxazaphospholane ring. The methyl group at the N1 atom (the torsion angles (C7C8N1C10) amount to −176.1(7) and 175.1(7)°) has an orientation close to that found in (II) and (III) (χ −162 and 171°, respectively).

The conformation of the 5-membered rings in the molecules of (IA) and (IB) is half-chair: the N1 and C8 atoms depart from the plane of the other atoms of the ring in different directions by 0.31 and 0.32 Å in (II) and by 0.29 and 0.32 Å in (IB) (see also the endocyclic torsion angles in Fig. 1). The C9 and C10 methyl groups are present in the equatorial orientation and deviate in the α- and β-directions, respectively, from this plane by

TABLE 1. Bond Lengths (Å) in the Molecule of 2e-Diethylamino-3e,4e-dimethyl-5e-phenyl-2a-thio-1,3,2-oxazaphospholane (I)

Angle	Molecule		Angle	Molecule	
	IA	IB		IA	IB
N1—P1	1,927 (3)	1,932 (2)	C1—C6	1,364 (7)	1,348 (7)
P1—O1	1,615 (3)	1,618 (3)	C1—C7	1,503 (7)	1,530 (7)
P1—S1	1,690 (4)	1,659 (4)	C2—C3	1,374 (8)	1,387 (8)
P1—N2	1,634 (4)	1,642 (4)	C3—C4	1,376 (9)	1,337 (9)
O1—C7	1,473 (6)	1,436 (6)	C4—C5	1,360 (8)	1,394 (8)
N1—C8	1,499 (6)	1,486 (6)	C5—C6	1,394 (8)	1,405 (8)
N1—C10	1,447 (6)	1,470 (7)	C7—C8	1,538 (7)	1,534 (7)
N2—C11	1,456 (7)	1,473 (7)	C8—C9	1,540 (7)	1,482 (7)
N2—C13	1,443 (6)	1,463 (7)	C11—C12	1,536 (8)	1,437 (9)
C1—C2	1,398 (7)	1,376 (7)	C13—C14	1,501 (8)	1,510 (10)

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*In the structural part of the paper (including Fig. 1 and Table 1), the numbering of the atoms in the molecule of (I) is taken to agree with the numbering in the molecule of d-pseudoephedrine and its derivatives.

Institute of Organic Synthesis and Coal Chemistry, Kazkh SSR Academy of Sciences, Karganda. A. N. Nesmeyanov Institute of Heteroorganic Compounds, USSR Academy of Sciences, Moscow. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 386-389, May-June, 1990. Original article submitted July 20, 1989; revision submitted December 28, 1989.

TABLE 2. Valence Angles (deg) in the Molecule of 2e-Diethylamino-3e,4e-dimethyl-5e-phenyl-2a-thio-1,3,2-oxazaphospholane

Angle	Molecule		Angle	Molecule	
	IA	IB		IA	IB
S1P1O1	114,0 (2)	113,3 (1)	C6C1C7	121,6 (4)	121,1 (4)
S1P1N1	117.1 (2)	118,5 (2)	C1C2C3	120,3 (5)	120,0 (5)
S1P1N2	114.6 (2)	114.6 (2)	C2C3C4	120,4 (5)	120,6 (6)
O1P1N1	94,7 (2)	94,2 (2)	C3C4C5	119.1 (5)	121,3 (6)
O1P1N2	106,6 (2)	107.9 (2)	C4C5C6	121,6 (5)	116,8 (5)
N1P1N2	107,8 (2)	106,3 (2)	C1C6C5	119,4 (5)	122,2 (5)
P1O1C7	113,6 (3)	112.9 (3)	O1C7C1	108,9 (4)	108,9 (4)
P1N1C8	106.9 (3)	108.9 (3)	O1C7C8	106,0 (4)	108,0 (4)
P1N1C10	117,7 (3)	118,1 (3)	C1C7C8	112,4 (4)	112,2 (4)
C8N1C10	118,2 (4)	115.4 (4)	N1C8C7	103,4 (4)	101,3 (4)
P1N2C11	123,5 (3)	121,0 (4)	N1C8C9	112,6 (4)	110,8 (4)
P1N2C13	120,7 (3)	119,1 (4)	C7C8C9	109,8 (4)	113,9 (4)
C11N2C13	115,8 (4)	119,0 (4)	N2C11C12	112.5 (4)	116,1 (5)
C2C1C6	119,3 (5)	119,1 (5)	N2C13C14	112,3 (4)	111,2 (5)
C2C1C7	119,1 (4)	119,8 (4)			

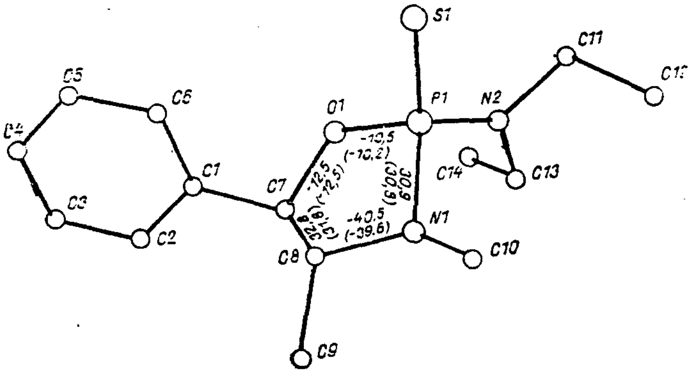

Fig. 1. Structure of the (IA) and (IB) molecules. The torsion angles in the 5-membered ring are given, those for (IB) being in parentheses.

0.29 and 0.12 Å in (IA) and 0.29 and 0.07 Å in (IB). The thiophosphoryl group, the phenyl substituent, and the diethylamino group have the β-,β- and α-orientations relative to the heterocycle, respectively; the deviations of the S1, C1, and N2 atoms from the mean plane of the ring amount to 1.63, 1.03, and 1.35 Å in (IA) and to 1.63, 1.03, and 1.37 Å in (IB).

The coordination of the phosphorus atom in the (IA) and (IB) molecules is distorted tetrahedral, the deviation of the valence angles from the ideal values corresponding to those found in other cyclic derivatives of tetracoordinated phosphorus [2, 3]. The coordination of the N2 atom is practically planar (the sums of the valence angles are 360.0 and 359.8° in (IA) and (IB), respectively).

The P1, N2, C11, and C13 atoms are coplanar with an accuracy of ±0.01 Å in (IA) and ±0.03 Å in (IB). The bond lengths and valence angles are the usual ones [4]. Only a pronounced shortening of the C11—C12 ordinary bond in the (IB) molecule to 1.437(9) A is observed, obviously because of the intensive thermal vibrations of the terminal ethyl group.

EXPERIMENTAL

The parameters of the cell and the intensities of 3116 reflections were measured on a Hilger-Watts automatic four-circle diffractometer (λ MoK, graphite monochromator, $\theta/2\theta$ scanning, $2\theta \leq 56°$). The crystals of (I) were monoclinic, a = 13.736(1), b = 7.848(1), c = 15.956(1) Å, β = 100.215(7)°, V = 1682.2(3) Å^3, M = 298.4, d_{calc} = 1.178 g/cm^3, Z = 4, $C_{14}H_{23}N_2OPS$, sp. gr. $P2_1$.

The calculations made use of 2565 independent reflections with $I \geq 3\sigma$. The structure was interpreted by the direct method using the SHELXTL program and was refined by block-diagonal MLS in the anisotropic approximation for the nonhydrogen atoms and the isotropic

TABLE 3. Coordinates of the Nonhydrogen Atoms ($\times 10^4$) in the Molecule of 2e-Diethylamino-3e,4e-dimethyl-5e-phenyl-2a-thio-1,3,2-oxazaphospholane (I)

Atom	Molecule (IA)			Molecule (IB)		
	x	y	z	x	y	z
S1	10639 (1)	5146	3809 (1)	4774 (1)	1748 (2)	6498 (1)
P1	9464 (1)	4271 (2)	3094 (1)	3094 (1)	3616 (2)	6981 (1)
O1	9509 (2)	4281 (4)	2084 (2)	5506 (2)	3712 (4)	7996 (2)
N1	9258 (3)	2152 (5)	3139 (2)	6760 (3)	3510 (5)	7122 (2)
N2	8444 (3)	5251 (5)	3201 (2)	5230 (3)	5499 (5)	6566 (2)
C1	10337 (4)	2533 (6)	1170 (3)	6301 (3)	2140 (7)	9236 (3)
C2	10153 (4)	1683 (7)	383 (3)	6795 (4)	2411 (7)	10059 (3)
C3	10872 (4)	1599 (8)	—118 (3)	6660 (4)	1301 (9)	10709 (3)
C4	11779 (5)	2351 (7)	149 (3)	6047 (4)	—29 (9)	10546 (3)
C5	11956 (4)	3667 (8)	918 (4)	5556 (4)	—378 (8)	9717 (4)
C6	11239 (4)	3267 (7)	1437 (3)	5689 (4)	791 (7)	9076 (3)
C7	9545 (3)	2566 (6)	1714 (1)	6449 (3)	3370 (7)	8521 (3)
C8	9764 (4)	1334 (6)	2478 (3)	7132 (3)	2631 (6)	7946 (3)
C9	9343 (4)	—441 (7)	2208 (4)	8195 (4)	3909 (8)	8245 (4)
C10	9369 (4)	1367 (8)	3976 (3)	7215 (4)	2966 (8)	6393 (3)
C11	8389 (4)	6533 (7)	3855 (3)	4390 (5)	5704 (8)	5853 (3)
C12	7982 (4)	5811 (9)	4623 (3)	3444 (5)	6025 (11)	6090 (6)
C13	7520 (4)	4841 (7)	2650 (3)	5743 (5)	7020 (7)	6951 (4)
C14	7231 (4)	6149 (9)	1961 (3)	6486 (6)	7658 (9)	6425 (5)

approximation for the H atoms (revealed in a difference synthesis) by the INEXT programs [6]. The final divergence factors were R = 0.044 and P_w = 0.032.

The system of coordinates was chosen in accordance with the known absolute configuration of d-pseudoephedrine [1]. The coordinates of the nonhydrogen atoms are given in Table 3. The coordinates of the H atoms and the values of the parameters of the thermal vibrations can be obtained from the authors.

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